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(η^4-CYCLOOCTA-1,5-DIENE)(η^6-CYCLOOCTA-1,3,5-TRIENE)RUTHENIUM(0): MECHANISTIC STUDY ON CARBONYLATION AND SYNTHESIS OF (η^4-CYCLOHEPTATRIENE)TRICARBONYLRUTHENIUM

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Summary

The carbonylation of Ru(η^4-C_8H_{12})(η^6-C_8H_{10}) (I) (C_8H_{12} = cycloocta-1,5-diene, C_8H_{10} = cycloocta-1,3,5-triene) occurs readily at room temperature and one atmosphere pressure of carbon monoxide. The initial product is Ru(CO)(η^4-C_8H_{12})(η^4-C_8H_{10}) (II); its formation was monitored by IR spectroscopy and shown to be first order with respect to I. Further reaction with CO produces $Ru(CO)_3$(η^4-C_8H_{12}). In the presence of C_7H_8 (C_7H_8 = cycloheptatriene) two major products are formed $Ru(CO)_3$(η^4-C_7H_8) and $Ru(CO)_2$(η^6-C_7H_8).

Introduction

Investigations of polyolefin metal carbonyl complexes of the iron triad [1] have revealed the importance of the ability of some derivatives of the type $M(CO)_3L$ to transfer the $M(CO)_3$ moiety to the polyolefin under mild conditions [2–6].

In extending our studies of [$Fe(CO)_3(C_7H_8)$] (BF_4) [7] to the ruthenium analogue, we had to synthesize $Ru(CO)_3$(η^4-C_7H_8) and we found its preparation either from direct reaction of $Ru_3(CO)_{12}$ with C_7H_8 [8] or via $Ru(CO)_3$(η^4-C_7H_8) [5] to be unsatisfactory.

We thus sought alternative routes to $Ru(CO)_3$(η^4-C_7H_8), and we now describe its synthesis by carbonylation of Ru(η^4-C_8H_{12})(η^6-C_8H_{10}) (I) [9–11] in the presence of cycloheptatriene. A mechanistic study of the first carbonylation product is also presented. Studies on the hydrogenation of I are described elsewhere [12].

Experimental

The complex $Ru(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_8H_{10})$ (I) was prepared as reported previously [11].

The kinetics of formation of the first carbonylation product were followed by monitoring the increase of the band at 1985 cm^{-1} in the IR spectrum of the reaction mixture. Rate data were calculated from a computer least-squares fit of values of $\ln(A_\infty - A_t)$ to time, where A_t and A_∞ are the absorbances at time t and after 7—8 half-lives, respectively. Uncertainties quoted are estimated standard errors. The activation parameters were calculated from a computer weighted least-squares fit of $\ln(k/T)$ to $1/T$, with the weighting scheme $w_i = (k_i/\sigma_i)^2$, where σ_i is the extimated standard error of k_i (correlation coefficient = —0.9936; uncertainties in activation parameters quoted are estimated standard errors).

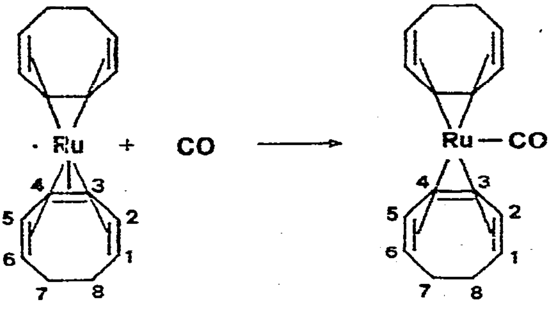
Solvents were dried and distilled under nitrogen before use. IR spectra were recorded at room temperature on a Perkin—Elmer Model 457 instrument and calibrated against polystyrene. ^1H NMR spectra were recorded on a Varian NV 14 spectrometer at 60 MHz. Chemical shifts refer to TMS as an internal standard.

For the ^1H NMR spectrum of $Ru(CO)(\eta^4\text{-}C_8H_{12})(\eta^4\text{-}C_8H_{10})$ (II), a 15 mg sample of I was dissolved in deuterobenzene in an NMR tube and treated with CO until the band at 1985 cm^{-1} no longer increased; a few drops of TMS were added and the spectrum was recorded. The other reaction mixtures referred to in the discussion were concentrated to small volumes and chromatographed on Al_2O_3 (reactivity 2) using petroleum ether (40—70°C) as eluent. The purity of the samples was checked by TLC, and by IR and ^1H NMR spectroscopy.

Results and discussion

Synthesis and kinetics of formation of $Ru(CO)(\eta^4\text{-}C_8H_{12})(\eta^4\text{-}C_8H_{10})$

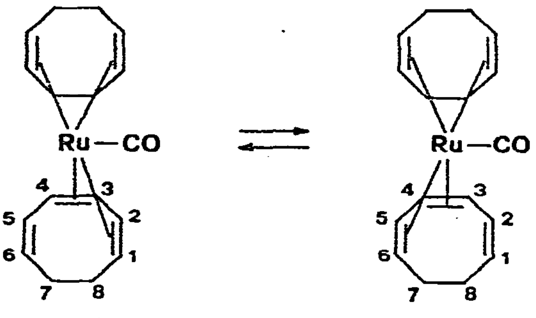
A n-hexane solution of $Ru(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_8H_{10})$ (I) absorbs carbon monoxide to give a pale-yellow solution having only one ν(CO) stretching frequency (1985 cm^{-1}) in the carbonyl region. Its ^1H NMR spectrum in C_6D_6 is very similar to that of I [11], with a substantial change only in the chemical shift of the multiplet attributed to H(3,4) (τ 4.05 ppm). The lowered value of the shift indicates release of the C(3)=C(4) bond in II from coordination to the metal. The up-



(I) (II)

field shift of protons attached to carbon—carbon double bonds upon coordination of a $M(CO)_x$ group (M = Fe, Ru) is well documented [13], and reflects increased electron density on the coordinated carbons. The formation of M—CO derivatives from polyolefinic complexes of ruthenium or osmium has been reported previously for complexes of the type $Ru(\eta^4\text{-NBD})(\eta^6\text{-}C_8H_8)$ [10] (NBD = bicyclo[2.2.1]hepta-2,5-diene; C_8H_8 = cycloocta-1,3,5,7-tetraene).

The possibility that the symmetric spectrum of II results from a rapid interconversion of two assymetric configurations of equivalent energy (IIa and IIb) can be rules out on the basis of absence of a shift of the signals due to H(1,2) and H(5,6) in II relative to those of I.



(IIa) (IIb)

The carbonylation of I to give II was assumed also to be first order in carbon monoxide, and the appropriate second order rate constants, k_2, were evaluated as $k_2 = k_{obs}/[CO]$. The CO concentration was taken as the solubility of the gas in n-heptane at 25°C [14] since the solubility in n-hexane is not available (this assumption is reasonable in view of the similarity of the solvents considered and the insensitivity of the solubility to changes in temperature in the limited range of temperatures examined). The rate data and activation parameters are listed in Table 1. The low activation enthalpy and largely negative entropy are consistent with an associative mechanism involving extensive loss of degrees of freedom and Ru—CO bond formation. All the results support the configuration III

TABLE 1

RATE DATA FOR THE REACTION

$Ru(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_8H_{10}) + CO \rightarrow Ru(CO)(\eta^4\text{-}C_8H_{12})(\eta^4\text{-}C_8H_{10})$

T (K)	k_{obs} (sec^{-1})	$k_2{}^a = \dfrac{k_{obs}}{[CO]}$ (M^{-1} sec^{-1})
266.16	1.32×10^{-3}	1.13×10^{-1}
289.16	4.34×10^{-3}	3.71×10^{-1}
312.16	1.5×10^{-2}	1.28

$\Delta H^{\star}$ = 8 ± 0.7 kcal/mol
$\Delta S^{\star}$ = —32 ± 2 e.u.

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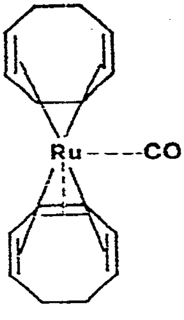
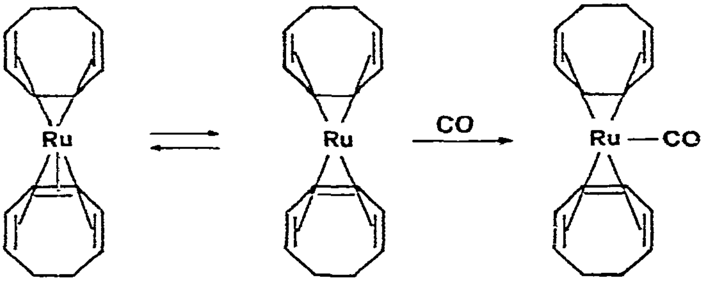
[a] $[CO] = 1.17 \times 10^{-2}$ M (calculated at 25°C) in n-heptane.

for the activated complex which is formed by direct interaction of I with CO.



(III)

However we must consider the alternative possibility that CO reacts with a species such as IV, which exists in labile equilibrium with I.



(I) (IV) (II)

Further reaction with CO

When CO is bubbled at room temperature into the reaction mixture containing complex II a slow reaction takes place which eventually gives $Ru(CO)_3$-$(\eta^4$-$C_8H_{12})$ (V) [5]. After 2 days the IR spectrum shows three bands in the ν(CO) region, at 2045, 1985, 1966 cm^{-1}, which agree well with reported values for that compound. The preferential detachment of η^4-C_8H_{10} rather than η^4-C_8H_{12} appears to be usual (see e.g. ref. 14).

If the carbonylation of I is carried out under the same conditions in the presence of an excess of cycloheptatriene (C_7H_8), the first step is again the formation of II. However further carbonylation does not give V, but a mixture which was separated by chromatography on Al_2O_3 with petroleum ether as eluent. After two minor pale yellow fractions * a major band is separated, which shows five IR bands at 2061, 2013, 1998, 1990(sh) and 1955 cm^{-1}. This fraction was concentrated to a small volume and again chromatographed on Al_2O_3. Elution with n-hexane gave two bands containing $[Ru(CO)_3(\eta^4$-CHT$)]$ (VI) (ν(CO) 2063, 1998, 1987 cm^{-1}) and $[Ru(CO)_2(\eta^6$-CHT$)]$ (VII) (ν(CO) 2012, 1954 cm^{-1}), respectively, in an approximate ratio of 4 to 1.

Further carbonylation of the reaction mixture before chromatography eventually gives $Ru_3(CO)_{12}$ which can be partially separated by filtration. Column

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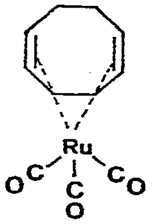
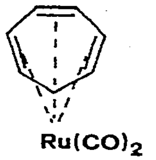
* No attempts are made to isolate compounds from these fractions.

cromatography of this reaction mixture also gives compounds of the type $[Ru_2(CO)_6(\eta^3,\eta^3\text{-}C_7H_8)]$ [8].

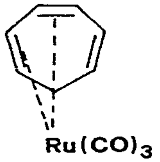
These results are consistent with the formation of $[Ru(CO)_3(\eta^4\text{-}C_8H_{12})]$ which eventually reacts with cycloheptatriene to give the corresponding complexes VI and VII.



(V)



(VII)



(VI)

The formation of $[Ru_2(CO)_6(\eta^6\text{-}C_7H_8)]$ after long time reactions is consistent with formation of the same product in the reaction of $Ru_3(CO)_{12}$ with cycloheptatriene.

The preparation of $[Ru(CO)_3(\eta^4\text{-}C_7H_8)]$ (VI) by this route has advantages over the reaction between $Ru(CO)_3(\eta^4\text{-}C_8H_{12})$ and cycloheptatriene. In particular there is no need to isolate the highly unstable $[Ru(CO)_3(\eta^4\text{-}C_8H_{12})]$, since the C_8H_{10} present in solution does not interfere with the subsequent reaction with C_7H_8. Furthermore the purification of VI at the end of the reaction presents no difficulty because of its stability.

Acknowledgments

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